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**EUROPEAN PATENT APPLICATION**

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**TECHNICAL FIELD**  
**BACKGROUND ART**

[0001] The present invention relates to a process for producing living radical polymers and the living radical polymers obtained by the process.

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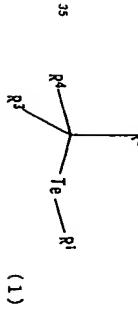
(71) **Applicant:** OTSUKA CHEMICAL COMPANY,  
LIMITED  
Osaka-shi, Osaka 540-0021 (JP)

(72) **Inventors:**

YAMAGO, Shigeru  
Kyoto-shi, Kyoto 606-8152 (JP)

**(54) PROCESS FOR PRODUCTION OF LIVING RADICAL POLYMERS AND POLYMERS**

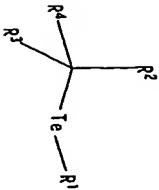
(57) A process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2), and the living radical polymer obtained by the process



(R<sup>1</sup>Te)<sub>2</sub>

(2)

wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>6</sub> alkyl, aryl substituted aryl or an aromatic heterocyclic group, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom or C<sub>1</sub>-C<sub>6</sub> alkyl, and R<sup>4</sup> is aryl substituted aryl, an aromatic heterocyclic group, acyl, oxycarbonyl or cyano



(1).

wherein R<sup>1</sup> is the same as above.

(R<sup>1</sup>Te)<sub>2</sub>

(2)

wherein R<sup>1</sup> is the same as above.

[0005] The living radical polymer of the present invention is produced by polymerizing a vinyl monomer in the presence of a compound represented by the formula (2) using a living radical polymerization initiator represented by the formula (1)

55



(4)  $M(R^1)_m$

wherein  $R^1$  is as defined above,  $M$  is an alkali metal, alkaline earth metal or copper atom, and  $m$  is 1 when  $M$  is an alkali metal,  $m$  is 2 when  $M$  is an alkaline earth metal, or  $m$  is 1 or 2 when  $M$  is a copper atom.

[0027] Examples of groups represented by  $R^1$  are as given above.

[0028] Examples of metals represented by  $M$  are lithium, sodium, potassium and like alkali metals, magnesium, calcium and like alkaline earth metals, and copper. Lithium is desirable.

[0029] In case that  $M$  is magnesium, the compound (4) may either be  $Mg(R^1)_2$  or a compound represented by  $MgX$  ( $X$  is a halogen atom) which is a Grignard reagent. Chlorine and bromine are preferable.

[0030] Examples of compounds usable are nethyl lithium, ethyl lithium, phenyllithium, p-methoxyphenyllithium, etc. Methyl lithium, ethyllithium, n-butyllithium and phenyllithium are preferable.

[0031] Next, a detailed description will be given of the process or preparing the compound.

[0032] Metallic tellurium is suspended in a solvent. Examples of solvents usable are dimethylformamide (DMF), tetrahydrofuran (THF) and like polar solvents, toluene, xylene and like aromatic solvents, hexane and like aliphatic hydrocarbons, dialkyl ethers and like ethers, etc. THF is preferable. The amount of solvent to be used, which is suitably adjusted, is 1 to 100 ml, preferably 5 to 10 ml, per gram of metallic tellurium.

[0033] A compound (4) is slowly added dropwise to the suspension, followed by stirring. The reaction time differs with the reaction temperature and pressure and is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is -20°C to 80°C, preferably 15°C to 40°C, more preferably room temperature. The reaction is conducted at increased pressure or in a vacuum.

[0034] Next, a compound (3) is added to the reaction mixture, followed by stirring. The reaction time differs with the reaction temperature and pressure and is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is -20°C to 80°C, preferably 15°C to 40°C, more preferably room temperature. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum.

[0035] The proportions of the compound (3) and compound (4) of metallic tellurium are 0.5 to 1.5, moles of the compound (3) and 0.5 to 1.5 moles of the compound (4), preferably 0.8 to 1.2 moles of the compound (3) and 0.8 to 1.2 moles of the compound (4), per mole of metallic tellurium.

[0036] After the completion of the reaction, the solvent is concentrated, and the desired compound is isolated and purified. Although the method of purification can be determined suitably depending on the compound, usually vacuum distillation or recrystallization is preferable.

[0037] The vinyl monomer to be used in the present invention is not particularly limited insofar as the monomer can be subjected to radical polymerization. Examples of vinyl monomers usable are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, (meth)acrylic acid 2-hydroxyethyl ester [2-hydroxyethyl (meth)acrylate] and like (meth)acrylic acid esters, cyclohexyl (meth)acrylate, methylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate and like cycloalkyl-containing unsaturated monomers, (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, crotonic acid, maleic anhydride and like carboxyl-containing unsaturated monomers, N,N-dimethylamino(meth)acryloyl (meth)acrylate, N,N-dimethylaminomethyl(meth)acrylate, N,N-dimethylamino(meth)acryloyl (meth)acrylate and like unsaturated monomers containing a tertiary amine, N-(2-hydroxy-2-acetoxyoxypropyl)-N,N,N-trimethylammonium chloride, N,N-dimethylbenzylammonium chloride and like unsaturated monomers containing quaternary ammonium base, glycidyl (meth)acrylate and like epoxy-containing unsaturated monomers, styrene,  $\alpha$ -methylstyrene, 4-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methoxystyrene, 2-hydroxystyrene, 2-chlorostyrene, 4-chlorostyrene, 2, $\beta$ -dichlorostyrene, 1-vinylnaphthalene, divinylbenzene, p-styrene sulfonic acid or an alkali metal salt thereof (sodium salt or potassium salt, etc.) and like aromatic unsaturated monomers (styrene type monomer, 2-vinylthiophene, N-methyl-2-vinylpyrrolidone and like unsaturated monomers containing a heterocyclic ring, N-vinylformamide, N-vinylacetamide and like vinylamides, 1-heptene, 1-decene and like  $\alpha$ -olefins, butadiene, isoprene, 4-methyl-1,4-hexadiene, 7-methyl-1,6-octadiene and like dienes, methyl vinyl ketone, ethyl vinyl ketone and like unsaturated monomers containing a carbonyl group, vinyl acetate, vinyl benzoate, hydroxyl(meth)acrylate, (meth)acrylonitrile, (meth)acrylamide, N-methyl(meth)acrylamide, N-isopropyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide and like (meth)acrylamide type monomers, vinyl chloride, etc.

[0038] Preferable among these are (meth)acrylic acid ester monomers, unsaturated monomers containing a tertiary amine, aromatic unsaturated monomers (styrene type monomers), unsaturated monomers containing a carbonyl group, acrylamide, (meth)acrylamide and N,N-dimethylacrylamide. Particularly preferable are (meth)acrylic acid ester monomers, aromatic unsaturated monomers (styrene type monomers), unsaturated monomers containing a carbonyl group, (meth)acrylonitrile, (meth)acrylamide type monomers.

propyl (methacrylate, butyl (methacrylate and (methacrylic acid 2-hydroxyethyl ester (methacrylate), acrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate and methacrylic acid 2-hydroxyethyl ester (hydroxymethyl) methacrylate).

[0040] Examples of preferable unsaturated monomers containing a tertiary amine are N,N-dimethylaminostyryl(methacrylate) and 2-dimethylaminostyryl(methacrylate).

[0041] Examples of preferable styrene type monomers are styrene,  $\alpha$ -methylstyrene,  $\alpha$ -methylstyrene, p-methoxystyrene,  $p$ -butylstyrene,  $p$ - $n$ -butylstyrene,  $p$ -chlorostyrene, and  $p$ -styrenesulfonic acid or an alkali metal salt thereof (sodium salt or potassium salt, etc.). More preferable are styrene,  $p$ -methoxystyrene and  $p$ -chlorostyrene.

The term "methacrylic acid" refers collectively to "acrylic acid" and "methacrylic acid".

[0042] Examples of compounds represented by the formula (2) and useful for the present invention are as follows wherein R<sup>1</sup> is the same as above.

[0043] The groups R<sup>1</sup> is the same as shown above.

[0044] Examples of preferred compounds represented by the formula (2) are those wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or phenyl.

[0045] More specific examples of compounds represented by the formula (2) are dimethyl ditelluride, diethyl ditelluride, di-n-propyl ditelluride, diisopropyl ditelluride, diisobutyl ditelluride, di-n-butyl ditelluride, di- $t$ -butyl ditelluride, di- $t$ -tert-butyl telluride, dicyclobutyl telluride, diphenyl ditelluride, bis( $p$ -methoxyphenyl) ditelluride, bis( $p$ -nitrophenyl) ditelluride, bis( $p$ -nitroanisyl) ditelluride, bis( $p$ -cyanophenyl) ditelluride, bis( $p$ -sulfonylphenyl) ditelluride, dipropyl ditelluride, dipropyl ditelluride, di- $t$ -butyl ditelluride, di- $t$ -butyl ditelluride, di-n-propyl ditelluride, diphenyl ditelluride, di- $t$ -butyl ditelluride, diethyl ditelluride, di- $t$ -butyl ditelluride, propyl ditelluride and di-n-butyl ditelluride.

[0046] Such compounds are prepared, for example, by reacting metallic tellurium with a compound represented by the formula (4).

[0047] Metallic tellurium is suspended in a solvent. Examples of solvents usable are dimethylformamide (DMF), tetrahydrofuran (THF) and like polar solvents, toluene, xylene and like aromatic solvents, hexane and like aliphatic solvents, and like non-polar solvents, chloroform, carbon tetrachloride, etc. The organic solvent is used usually in an amount of about 10 times the amount of tellurium.

an amount of 1 to 100 ml, preferably 5 to 10 ml, per gram of metallic tellurium although the amount is suitably adjustable.

[0048] The compound represented by the formula (4) is slowly added dropwise to the suspension, followed by stirring. The reaction time is usually 5 minutes to 24 hours, although varying with the reaction temperature and pressure. The reaction temperature is -20°C to 80°C, preferably 15°C to 40°C, more preferably room temperature. The reaction is conducted usually at atmospheric pressure, but an increased or reduced pressure is usable.

[0049] Subsequently, water (which may be neutral water such as saline solution, alkali water such as aqueous solution of ammonium chloride, or acid water such as aqueous solution of hydrochloric acid) is added to the reaction mixture, followed by stirring. Although varying with the reaction temperature or pressure, the reaction time is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is -20°C to 80°C, preferably 15°C to 40°C, more preferably room temperature. The reaction is conducted usually at atmospheric pressure, but an increased or reduced pressure is usable.

[0050] Metallic tellurium and the compound of the formula (4) are used in such a ratio that 0.5 to 1.5 moles, preferably 0.8 to 1.2 moles, of the compound of the formula (4) is used per mole of metallic tellurium.

[0051] After the completion of the reaction, the solvent is concentrated, and the desired product is isolated from the concentrate and purified. Although the compound can be purified by a suitable selected method, vacuum distillation or reprecipitation purification is usually desirable.

[0052] Specifically stated, the living radical polymer of the present invention is produced by the process to be described below.

[0053] A vinyl monomer, a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2), are mixed together in a container having its inside air replaced by an inert gas. At this time, the initiator represented by the formula (1) and the compound of the formula (2) may be mixed together by stirring as the first step, followed by the second step of adding the vinyl monomer to the mixture. Examples of inert gases usable at this time are nitrogen, argon, helium, etc., among which argon and nitrogen are preferred. Nitrogen is especially preferred.

[0054] Although the vinyl monomer and the initiator represented by the formula (1) are used in amounts which are suitably adjusted depending on the molecular weight and molecular weight distribution of the living radical polymer to be obtained, usually 5 to 10,000 moles, preferably 50 to 5,000 moles, of the vinyl monomer is used per mole of the initiator represented by the formula (1).

[0055] To obtain a preferred mixture of living radical polymerization initiator of the formula (1) and compound of the formula (1) wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>4</sub> alkyl, R<sub>2</sub> and R<sub>3</sub> are each a hydrogen atom or C<sub>1</sub>-C<sub>4</sub> alkyl, and R<sub>4</sub> is aryl, substituted aryl or oxy carbonyl and a compound of the formula (2) wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>4</sub> alkyl or phenyl.

[0056] The living radical polymerization initiator represented by the formula (1) and the compound represented by the formula (2) are used in the ratio of usually 0.1 to 100 moles, preferably 0.5 to 100 moles, more preferably 1 to 10 moles, especially preferably 1 to 5 moles, of the compound of the formula (2) per mole of the initiator of the formula (1). [0057] The polymerization reaction is conducted usually in the absence of solvent, while an organic solvent generally in use for radical polymerization may be used. Examples of solvents usable are benzene, toluene, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, chloroform, carbon tetrachloride, tetrahydrofuran (THF), ethyl acetate, trifluoromethylbenzene, etc. Aqueous solvents are also usable which include, for example, water, methanol, ethanol, isopropanol, n-butanol, ethyl cellosolve, butyl cellosolve, 1-methoxy-2-propanol, etc. The amount of the solvent to be used is adjusted suitably. For example, 0.01 to 0.01 to 10 ml, preferably 0.05 to 0.5 ml, of the solvent is used per gram of the vinyl monomer.

[0058] Next, the mixture is then stirred. The reaction temperature and the reaction time may be adjusted suitably in accordance with the molecular weight or molecular weight distribution of the living radical polymer to be obtained. The mixture is stirred usually at 60 to 150°C for 5 to 100 hours, preferably at 80 to 120°C for 10 to 30 hours. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum.

[0059] After the completion of the reaction, the solvent used and the remaining monomer are removed in a vacuum to take out the desired polymer, or the desired product is isolated by reprecipitation using a solvent wherein the product is insoluble. The reaction mixture can be treated by any method insofar as it causes no problem to the desired product. [0060] Different kinds of vinyl monomers are usable in the process of the invention for preparing a living radical polymer. For example, when at least two kinds of vinyl monomers are reacted at the same time, a random copolymer can be obtained. The random copolymer obtained is a polymer which comprises the reacted monomers in the original ratio (mole ratio) regardless of the kinds of the monomers. When a random copolymer is obtained by reacting a vinyl monomer A and a vinyl monomer B at the same time, the copolymer has substantially the same material ratio (mole ratio). Further, when two kinds of vinyl monomers are reacted in succession, a block copolymer can be obtained. The block copolymer is provided by the same order of reacted monomers regardless of the kinds of the monomers. If a vinyl monomer A and a vinyl monomer B are reacted in succession to obtain a block copolymer, the polymer obtained

is in the order of A-B or B-A in conformity with the order of monomers reacted.

[0061] The living radical polymerization initiator of the present invention is adapted for excellent control of molecular weights and molecular weight distributions under very mild conditions.

[0062] The living radical polymer to be obtained by the invention is adjustable in molecular weight according to the reaction time, the amount of the living radical polymerization initiator (organotellurium compound) of the formula (1) and the amount of the compound of the formula (2), and can be 500 to 1,000,000 in number average molecular weight. This invention is especially suitable for producing living radical polymers having a number average molecular weight of 10,000 to 500,000, more preferably 1,000 to 50,000.

[0063] The living radical polymer to be obtained by the invention is controlled to 1.05 to 1.50 in molecular weight distribution ( $P_D = M_w/M_n$ ). The molecular weight distribution is controllable to a narrower range of 1.05 to 1.30, a further narrower range of 1.05 to 1.20, a still narrower range of 1.05 to 1.15.

[0064] It has been found that the living radical polymer of the present invention has a terminal group which is an alky, aryl, substituted aryl, aromatic heterocyclic group, acyl, oxy carbonyl or cyano derived from the organotellurium compound and a growth terminal which is highly reactive tellurium. Accordingly, the organotellurium compound used for radical polymerization makes it easier to convert the terminal group to other functional group than in the case of the living radical polymer obtained by conventional living radical polymerization. The living radical polymer obtained according to the invention is therefore useable as a macro living radical polymerization initiator (macroinitiator).

[0065] A-B diblock copolymers such as methyl methacrylate-styrene and B-A diblock copolymers such as styrene-methyl methacrylate can be obtained using a macro living radical polymerization initiator of the invention. A-B-A triblock copolymers such as methyl methacrylate-styrene-methyl methacrylate and A-B-C triblock copolymers such as methyl methacrylate-styrene-butyl acrylate are also available. This is attributable to the fact that the vinyl monomers of various different types are controllable by the living radical polymerization initiator and the dilute tellurium compound of the invention, and also to the fact that highly reactive tellurium is present at the growth terminal of the living radical polymer obtained with use of the living radical polymerization initiator.

[0066] Stated more specifically, block copolymers are prepared by the processes to be described below.

[0067] For preparing A-B diblock copolymers such as methyl methacrylate-styrene copolymer, methyl methacrylate, a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2) are mixed together first as in the process described above for preparing a living radical polymer to obtain poly(methyl methacrylate), and subsequently mixing styrene with the polymer to obtain methyl methacrylate-styrene copolymer.

[0068] A-B-A triblock copolymers and A-B-C triblock copolymers can be produced, for example, by preparing an A-B diblock copolymer by the above process, and thereafter mixing a vinyl monomer (A) or vinyl monomer (C) with the copolymer to obtain the A-B-A or A-B-C triblock copolymer.

[0069] In producing the diblock copolymer according to the invention, the compound of the formula (1) and the compound of the formula (2) can be used when a homopolymer is prepared from the first monomer and/or when the diblock copolymer is subsequently prepared.

[0070] Further, in producing the triblock copolymer according to the invention the compound of the formula (1) and the compound of the formula (2) can be used at least once when a homopolymer is prepared from the first monomer, or when a diblock copolymer is subsequently prepared, or when the triblock copolymer is subsequently prepared.

[0071] The preparation of each block may be followed directly by the subsequent reaction for the next block, or the subsequent reaction for the next block may be initiated after the purification of the product resulting from the completion of the first reaction. The block copolymer can be isolated by a usual method.

## BEST MODE OF CARRYING OUT THE INVENTION

[0072] The present invention will be described below in detail with reference to Examples, but is not limited thereto in any way. In Examples and Comparative Examples, properties were determined by the following methods.

### (1) Identification of organotellurium compounds and living radical polymers

[0073] The organotellurium compound was identified based on the results of <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR and MS analyses. The molecular weight and molecular weight distribution of the living radical polymer were determined using GPC (gel permeation chromatography). The measuring instruments used are as follows.

<sup>1</sup>H-NMR : Varian Gemini 2000, JEOL JNM-A400 (400MHz for <sup>1</sup>H)

<sup>13</sup>C-NMR : Varian Gemini 2000, JEOL JNM-A400 (300MHz for <sup>13</sup>C)

IR : Shimadzu FTIR-8200 (cm<sup>-1</sup>)

MS (HRMS) : JEOL JMS-300

Molecular weight and molecular weight distribution : liquid chromatography Shimadzu LC-10 (column : Shodex K-804 + K-805L, polystyrene standard : TOSOH TSK Standard, poly(methyl methacrylate) standard : Shodex Standard M-75)

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**Preparation Example 1****Preparation of (1-methyltellanyl-ethyl)benzene**

[0074] A 6.38 g quantity (50 mmoles) of metallic tellurium [product of Aldrich, brand name: Tellurium (40 mesh)] was suspended in 50 ml of THF, and 52.9 g/ml (1.04 M dieethyl ether solution, 50 ml) of methyl lithium [product of Kanto Chemical Co., Ltd. dieethyl ether solution] was slowly added dropwise to the suspension at room temperature (for 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 11.0 g (60 mmoles) of (1-bromoethyl)benzenes at room temperature, followed by stirring for 2 hours. After the completion of reaction, the solvent was concentrated in a vacuum, followed by vacuum distillation to give 8.66 g of yellow oil (70% in yield).

[0075] IR, HRMS,  $^{1}\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analyses indicated that the product was (1-methyltellanyl-ethyl)benzene. IR(neat,  $\text{cm}^{-1}$ ): 1599, 1493, 1451, (3175, 1219, 1140, 930, 760, 686, 577 HRMS(ESI) m/z: 259, 250, 00011  $^{1}\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 1.78 (s, 3H,  $\text{TeCH}_3$ ), 1.90 (d,  $J=7.2\text{Hz}$ , 3H), 4.57 ( $\text{q}, J=7.2\text{Hz}$ , 1H,  $\text{CHTe}$ ), 7.08-7.32 (m, 5H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ) -18.94, 18.30, 23.89, 126.17, 126.80, 128.30, 145.79

**Preparation Example 2****Preparation of ethyl-2-methyl-2-methytellanyl-propionate**

[0076] The same procedure as in Preparation Example 1 was performed with the exception of using 10.7 g (55 mmoles) of allyl-2-bromo-isobutyrate in place of (1-bromoethyl)benzenes to obtain 6.53 g (51% in yield) of yellow oil. [0077] IR, HRMS,  $^{1}\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analyses indicated that the product was ethyl-2-methyl-2-methytellanyl-propionate. IR(neat,  $\text{cm}^{-1}$ ): 1700, 1466, 1386, 1269, 1146, 1111, 1028 HRMS(ESI) m/z: Calcd for  $\text{C}_8\text{H}_{12}\text{O}_2\text{Te}(\text{M})^+$ : 260.0056; Found 260.0053  $^{1}\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 1.27 (t,  $J=6.9\text{Hz}$ , 3H), 1.74 (s, 5H,  $\text{TeCH}_3$ ), 4.16 (q,  $J=7.2\text{Hz}$ , 2H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ) -17.38, 13.89, 23.42, 27.93, 60.80, 176.75

**Preparation Example 3 dimethyl telluride**

[0078] A 3.19 g quantity (25 mmoles) of metallic tellurium (the same as above) was suspended in 25 ml of THF, and 25 ml (28.5 mmoles) of methyl lithium (the same as above) was added slowly to the suspension at  $0^\circ\text{C}$  (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 10 minutes). To the resulting reaction mixture was added 20 ml of a solution of ammonium chloride at room temperature. The organic layer was subjected to extraction with dichloro ether 3 times. The organic layers were collected, dried over anhydrous sodium sulfate and concentrated in a vacuum, affording 2.69 g (9.4 mmoles, yield 75% of blackish purple oil.

[0079] The product was found to be dimethyl telluride by MS (HRMS) and  $^{1}\text{H-NMR}$ , HRMS(ESI) m/z: Calcd for  $\text{C}_2\text{H}_6\text{Te}_2(\text{M})^+$ : 289.8534; Found 289.8533  $^{1}\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 2.67 (s, 6H)

**Preparation Example 4 (diphenyl telluride)**

[0080] A 3.19 g quantity (25 mmoles) of metallic tellurium (the same as above) was suspended in 25 ml of THF, and 15.5 ml (28.5 mmoles) of phenyllithium [product of Aldrich, 1.8M cyclohexane/ether (70/30) solution] was added slowly to the suspension at  $0^\circ\text{C}$  (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 10 minutes). To the resulting reaction mixture was added 20 ml of a solution of ammonium chloride at room temperature, followed by stirring for 1 hour. The organic layer was separated off, and the aqueous layer was subjected to extraction with diethyl ether 3 times. The organic layers were collected, dried over anhydrous sodium sulfate and concentrated in a vacuum, affording 3.48 g (8.5 mmoles, yield 68%) of blackish purple oil.

[0081] The product was found to be diphenyl telluride by MS (HRMS) and  $^{1}\text{H-NMR}$ .

**Examples 1 to 4****Preparation of poly(methyl methacrylate)**

[0082] Along with 24.8 mg (0.10 mmole) of the (1-methyltellanyl-ethyl)benzene prepared in Preparation Example 1, methyl methacrylate (stabilized with hydroquinone (HQ)) and a solution of the dimethyl telluride prepared in Preparation Example 1 shows the result of GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)).

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ratiion Example 3 were placed in the ratio listed in Table 1 into a glove box with the inside air replaced by nitrogen, followed by stirring. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 250 ml of hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried to obtain poly(methyl methacrylate).

5 [0083] Table 1 shows the result of GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)).

Table 1

	Ex.	methyl methacrylate	dimethyl telluride	reaction condition	yield (%)	Mn	PD
10	1	1.01 g (10 mmol)	28.5 mg (0.10 mmol)	80 °C 13 h	92	9700	1.16
15	2	2.02 g (20 mmol)	28.5 mg (0.10 mmol)	80 °C 13 h	83	16100	1.14
15	3	5.05 g (50 mmol)	57.0 mg (0.20 mmol)	80 °C 18 h	79	36300	1.18
15	4	10.10 g (100 mmol)	57.0 mg (0.20 mmol)	80 °C 24 h	83	79400	1.14

**Comparative Example 1****Preparation of poly(methyl methacrylate)**

20 [0084] Poly(methyl methacrylate) was prepared in the same manner as in Example 1 except that no dimethyl telluride was used (67% in yield).

[0085] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 8100 and PD=1.77.

[0086] A comparison between Example 1 and Comparative Example 1 indicates that when dimethyl telluride was used as a compound represented by the formula (2), a living radical polymer of narrower molecular weight distribution (PD value closer to 1) is obtained.

25 Example 5

Preparation of poly(methyl methacrylate)
Preparation of poly(methyl methacrylate)

[0087] A 25.8 mg quantity (0.10 mmole) of the allyl-2-methyl-2-methytellanyl-propionate prepared in Preparation Example 2, 1.01 g (10 mmole) of methyl methacrylate and a solution of 28.5 mg (0.10 mmole) of the dimethyl telluride prepared in Preparation Example 3 were stirred at 80°C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.85 g (yield 84%) of poly(methyl methacrylate).

[0088] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 8200 and PD=1.12.

40 Example 6

Preparation of poly(methyl methacrylate)
Preparation of poly(methyl methacrylate)

[0089] A 25.8 mg quantity (0.10 mmole) of the ethyl-2-methyl-2-methytellanyl-propionate prepared in Preparation Example 2, 1.14 g (10 mmole) of ethyl methacrylate (stabilized with HQ) and a solution of 28.5 mg (0.10 mmole) of the dimethyl telluride prepared in Preparation Example 3 were stirred at 105°C for 2 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 1.11 g (yield 97%) of poly(methyl methacrylate).

55 [0090] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 10600 and PD=1.12.

**Example 7**Preparation of poly(2-hydroxyethyl methacrylate)

**5** [0091] In 1 ml of N,N-dimethylformamide (DMF) were dissolved 25.8 mg (0.10 mmole) of the ethyl-2-methoxyethyl methacrylate (stabilized with hydroquinone methyl ether (MEOQ)) and 28.5 mg (0.10 mmole) of the dimethyl tellurium prepared in Preparation Example 3 in a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the solvent was removed by distillation in a vacuum, affording 1.28 g (yield 57%) of poly(2-hydroxyethyl methacrylate).

**[0092]** GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 22300 and PD=1.27.

**Example 8**Preparation of polystyrene

**[0093]** A 24.8 mg quantity (0.10 mmole) of the (1-methylethyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (1.0 mmole) of styrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl tellurium prepared in Preparation Example 3 were stirred at 120°C for 1.4 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 1.01 g (yield 97%) of polystyrene. (reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 9000 and PD=1.18.

**Example 9**Preparation of polystyrene

**[0095]** A 24.8 mg quantity (0.10 mmole) of the (1-methylethyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (1.0 mmole) of styrene and a solution of 40.9 mg (0.10 mmole) of the diphenyl telluride prepared in Preparation Example 4 were stirred at 120°C for 1.4 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.99 g (yield 95%) of polystyrene. (reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 9200 and PD=1.13.

**Example 10**Preparation of poly(methyl methacrylate-b-styrene) diblock polymer

**[0097]** A 1.01 g quantity (10 mmole) of the (1-methylethyl-ethyl)benzene prepared in Preparation Example 1 and 28.5 mg (0.10 mmole) of the dimethyl tellurium prepared in Preparation Example 3 were reacted at 100°C for 24 hours in a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of deuteriochloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.765 g (yield 65%) of poly(methyl methacrylate).

**[0098]** GPC analysis revealed Mn 8500 and PD=1.12.

**[0099]** Next, 425 mg (0.05 mmole) of the poly(methyl methacrylate) [used as a macronitiator] obtained above and 520 mg (5 mmole) of styrene were reacted at 100°C for 24 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.5553 g (yield 57%) of poly(methyl methacrylate-b-styrene) diblock polymer. GPC analysis revealed Mn 18700 and PD=1.18.

**Preparation Example 6**Preparation of 1-(1-methylethyl-ethyl)-4-trifluoromethylbenzene

**[0100]** A 4.08 g quantity (32 mmole) of metallic tellurium (the same as above) was suspended in 50 ml of THF, and 29.2 ml (35 mmoles of 1.20M diethyl ether solution) of methyl lithium was slowly added dropwise to the suspension at 0°C (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 5 minutes). To the reaction mixture was added 7.88 g (35 mmoles) of 1-(1-bromoethyl)-4-chlorobenzene at 0°C, followed by stirring at room temperature for 1.5 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was then distilled in a vacuum, giving 3.59 g (yield 40%) of orange oil.

**[0101]** IR, HRMS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicated that the product was 1-(chloro-4-(1-methylethyl-ethyl)benzene, IR (neat, cm<sup>-1</sup>) 1891, 1686, 1489, 1408, 928 HRMS (EI) m/z : Calcd for C<sub>9</sub>H<sub>11</sub>ClTe(M)<sup>+</sup>, 283.9612; Found 283.9601

**[0102]** A 5.74 g quantity (45 mmole) of metallic tellurium (the same as above) was suspended in 60 ml of THF, and 45.5 ml (50 mmoles of 1.10M diethyl ether solution) of methyl lithium was slowly added dropwise to the suspension at 0°C (over a period of 10 minutes). The reaction mixture disappeared until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 11.4 g (45 mmoles) of 1-(1-bromoethyl)-4-trifluoromethylbenzene at 0°C, followed by stirring at room temperature for 1.5 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was then distilled in a vacuum, giving 2.40 g (yield 17%) of yellow oil.

**[0103]** IR, HRMS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicated that the product was 1-(1-methylethyl-ethyl)-4-trifluoromethylbenzene.

**Preparation Example 5**Preparation of 1-chloro-4-(1-methylethyl-ethyl)benzene

**5** [0091] In 1 ml of N,N-dimethylformamide (DMF) were dissolved 25.8 mg (0.10 mmole) of the ethyl-2-methoxyethyl methacrylate prepared in Preparation Example 2, 1.30 g (1.0 mmole) of 2-hydroxyethyl methacrylate (stabilized with hydroquinone methyl ether (MEOQ)) and 28.5 mg (0.10 mmole) of the dimethyl telluride prepared in Preparation Example 3 in a glove box having its inside air replaced by nitrogen. The solution was stirred at 80°C for 8 hours. After the completion of the reaction, the solvent was removed by distillation in a vacuum, affording 1.28 g (yield 57%) of poly(2-hydroxyethyl methacrylate), revealed Mn 22300 and PD=1.27.

**[0092]** GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 22300 and PD=1.27.

**Example 8**Preparation of polystyrene

**[0093]** A 24.8 mg quantity (0.10 mmole) of the (1-methylethyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (1.0 mmole) of styrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl tellurium prepared in Preparation Example 3 were stirred at 120°C for 1.4 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 1.01 g (yield 97%) of polystyrene. (reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 9000 and PD=1.18.

**Example 9**Preparation of polystyrene

**[0095]** A 24.8 mg quantity (0.10 mmole) of the (1-methylethyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (1.0 mmole) of styrene and a solution of 40.9 mg (0.10 mmole) of the diphenyl telluride prepared in Preparation Example 4 were stirred at 120°C for 1.4 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.99 g (yield 95%) of polystyrene. (reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 9200 and PD=1.13.

**Example 10**Preparation of poly(methyl methacrylate-b-styrene) diblock polymer

**[0097]** A 1.01 g quantity (10 mmole) of the (1-methylethyl-ethyl)benzene, 24.8 mg (0.10 mmole) of the (1-methylethyl-ethyl)benzene prepared in Preparation Example 1 and 28.5 mg (0.10 mmole) of the dimethyl tellurium prepared in Preparation Example 3 were reacted at 100°C for 24 hours in a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of deuteriochloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.765 g (yield 65%) of poly(methyl methacrylate).

**[0098]** GPC analysis revealed Mn 8500 and PD=1.12.

**[0099]** Next, 425 mg (0.05 mmole) of the poly(methyl methacrylate) [used as a macronitiator] obtained above and 520 mg (5 mmole) of styrene were reacted at 100°C for 24 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording 0.5553 g (yield 57%) of poly(methyl methacrylate-b-styrene) diblock polymer. GPC analysis revealed Mn 18700 and PD=1.18.

**Preparation Example 8**Preparation of 1-(1-methylethyl-ethyl)-4-trifluoromethylbenzene

**[0100]** A 4.08 g quantity (32 mmole) of metallic tellurium (the same as above) was suspended in 50 ml of THF, and 29.2 ml (35 mmoles of 1.20M diethyl ether solution) of methyl lithium was slowly added dropwise to the suspension at 0°C (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 5 minutes). To the reaction mixture was added 7.88 g (35 mmoles) of 1-(1-bromoethyl)-4-chlorobenzene at 0°C, followed by stirring at room temperature for 1.5 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was then distilled in a vacuum, giving 3.59 g (yield 40%) of orange oil.

**[0101]** IR, HRMS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicated that the product was 1-(chloro-4-(1-methylethyl-ethyl)benzene, IR (neat, cm<sup>-1</sup>) 1891, 1686, 1489, 1408, 928 HRMS (EI) m/z : Calcd for C<sub>9</sub>H<sub>11</sub>ClTe(M)<sup>+</sup>, 283.9612; Found 283.9601

**[0102]** A 5.74 g quantity (45 mmole) of metallic tellurium (the same as above) was suspended in 60 ml of THF, and 45.5 ml (50 mmoles of 1.10M diethyl ether solution) of methyl lithium was slowly added dropwise to the suspension at 0°C (over a period of 10 minutes). The reaction mixture disappeared until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 11.4 g (45 mmoles) of 1-(1-bromoethyl)-4-trifluoromethylbenzene at 0°C, followed by stirring at room temperature for 1.5 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was then distilled in a vacuum, giving 2.40 g (yield 17%) of yellow oil.

**[0103]** IR, HRMS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicated that the product was 1-(1-methylethyl-ethyl)-4-trifluoromethylbenzene.

42.0 ml (50 mmoles of 1.20M diethyl ether solution) of methyl lithium was slowly added dropwise to the suspension at 0°C (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (30 minutes). To the reaction mixture was added 12.4 g (45 mmoles) of 1,2,3,4,5-pentafluoro-6-(1-bromoethyl)benzene at 0°C, followed by stirring at room temperature for 2 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was then distilled in a vacuum, giving 2.65 g (yield 19%) of orange oil.

[0107] IR, HRMS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicated that the product was 1,2,3,4,5-pentafluoro-6-(1-methyltellanyl-ethyl)benzene. [IR(neal, cm<sup>-1</sup>) 1653, 1522, 1499, 1144, 1075, 1048, 984, 903 HRMS (El) m/z: Calcd for C<sub>9</sub>H<sub>7</sub>F<sub>5</sub>Ta(M)<sub>1</sub>: 339.9535; <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) 1.93(s, 3H, J=7.2Hz, 3H), 2.05(s, 3H, J=7.5Hz, 1H); <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>) 19.07, 2.01, 22.38, 120.79-121.14(m), 137.55(d,dd, J<sub>C,F</sub>=26 Hz), 139.52 (dt, J<sub>C,F</sub>=249 Hz), 143.38(dm, J<sub>C,F</sub>=248 Hz).

#### Preparation Example 9

##### Preparation of 1-methoxy-4-(1-methyltellanyl-ethyl)benzene

[0108] A 7.65 g quantity (60 mmoles) of metallic tellurium (the same as above) was suspended in 50 ml of THF, and 55.0 ml (68 mmoles of 1.20M diethyl ether solution) of methyl lithium was slowly added dropwise to the suspension at 0°C (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (30 minutes). To the reaction mixture was added 12.9 g (60 mmoles) of 1-(1-bromoethyl)-6-methoxybenzene at 0°C, followed by stirring at room temperature for 1.5 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was then distilled in a vacuum, giving 10.8 g (yield 40%) of orange oil.

[0109] IR, HRMS, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR indicated that the product was 1-methoxy-4-(1-methyltellanyl-ethyl)benzene. [IR(neal, cm<sup>-1</sup>) 1609, 1509, 1248, 1177, 1040, 830 HRMS (El) m/z: Calcd for C<sub>10</sub>H<sub>14</sub>Ota(M)<sub>1</sub>: 281.0106

[0110] <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>) 1.78(s, 3H), 1.85(d, J=7.2Hz, 3H), 4.58(q, J=7.3Hz, 1H), 6.83(d, J=8.4Hz, 2H), J=9.0Hz, 2H)

[0111] <sup>13</sup>C-NMR(100MHz, CDCl<sub>3</sub>) -18.98, 17.94, 24.30, 55.23, 113.70, 127.86, 137.95, 157.84.

#### Preparation Example 10

##### Preparation of ethyl-2-methyl-2-n-butyltellanyl-propionate

[0112] A 3.19 g quantity (50 mmoles) of metallic tellurium (the same as above) was suspended in 50 ml of THF, and 34.4 ml (55 mmoles) of n-butyl lithium (product of Aldrich, 1.6M hexane solution) was slowly added dropwise to the metallic suspension at room temperature (over a period of 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 10.7 g (55 mmoles) of ethyl-tellurium bisobutylate at room temperature, followed by stirring for 2 hours. After the completion of the reaction, the solvent was concentrated in a vacuum, and the concentrate was subsequently distilled in a vacuum, giving 8.98 g (yield 59.5%) of yellow oil.

[0113] <sup>1</sup>H-NMR indicated that the product was ethyl-2-methyl-2-n-butyltellanyl-propionate. [IR(neal, cm<sup>-1</sup>) 3030, 2950, 1727, 1593, 1493, 1453, 1377, 1250, 1130, 1090, 1050, 980, 900, 850, 750, 650, 550, 450, 350, 250, 150, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, 4, 3, 2, 1 Hz]

[0114] A 28.4 mg quantity (0.10 mmole) of the 1-chloro-4-(1-methyltellanyl-ethyl)-4-trifluoromethylbenzene prepared in Preparation Example 5, 1.01 g (10 mmoles) of methyl methacrylate and a solution of 28.5 mg (0.10 mmole) of the dimethyl dilithium prepared in Preparation Example 3 were stirred at 80°C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate) in a yield of 71%.

[0115] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 6800 and PD=1.12.

#### Example 11

##### Preparation of poly(methyl methacrylate)

[0116] A 31.8 mg quantity (0.10 mmole) of the 1-(1-methyltellanyl-ethyl)-4-trifluoromethylbenzene prepared in Preparation Example 6, 1.01 g (10 mmoles) of methyl methacrylate and a solution of 28.5 mg (0.10 mmole) of the dimethyl dilithium prepared in Preparation Example 3 were stirred at 80°C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate) in a yield of 93%.

[0117] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 6800 and PD=1.12.

##### Preparation of poly(methyl methacrylate)

[0118] A 38.6 mg quantity (0.10 mmole) of the 1-(1-methyltellanyl-ethyl)-3,5-trifluoromethylbenzene prepared in Preparation Example 7, 1.01 g (10 mmoles) of methyl methacrylate and a solution of 28.5 mg (0.10 mmole) of the dimethyl dilithium prepared in Preparation Example 3 were stirred at 80°C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate) in a yield of 69%.

[0119] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 6800 and PD=1.11.

#### Example 12

##### Preparation of poly(methyl methacrylate)

[0120] A 34.0 mg quantity (0.10 mmole) of the 1,2,3,4-pentafluoro-6-(1-methyltellanyl-ethyl)benzene prepared in Preparation Example 8, 1.01 g (10 mmoles) of methyl methacrylate and a solution of 28.5 mg (0.10 mmole) of the dimethyl dilithium prepared in Preparation Example 3 were stirred at 80°C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate) in a yield of 44%.

[0121] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 5200 and PD=1.25.

##### Preparation of poly(methyl methacrylate)

prepared in Preparation Example 3 were stirred at 80°C for 13 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate) in a yield of 63%.

#### Example 16

##### Preparation of polystyrene

[0124] A 24.8 mg quantity (0.10 mmole) of the (1-methylallyl-ethyl)benzene prepared in Preparation Example 1, 1.04 g (10 mmoles) of styrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl diellulide prepared in Preparation Example 3 were stirred at 100°C for 20 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording polystyrene in a yield of 74%.

[0125] GPC analysis (with reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 6500 and PD=1.17.

#### Example 17

##### Preparation of polystyrene

[0126] A 28.4 mg quantity (0.10 mmole) of the 1-chloro-4-(1-methylallyl-ethyl)benzene prepared in Preparation Example 5, 1.04 g (10 mmoles) of styrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl diellulide prepared in Preparation Example 3 were stirred at 100°C for 20 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording polystyrene in a yield of 75%.

#### Example 18

##### Preparation of poly(p-chlorostyrene)

[0128] A 24.8 mg quantity (0.10 mmole) of the (1-methylallyl-ethyl)benzene prepared in Preparation Example 1, 1.39 g (10 mmoles) of p-chlorostyrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl diellulide prepared in Preparation Example 3 were stirred at 100°C for 17 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(p-chlorostyrene) in a yield of 92%.

#### Example 19

##### Preparation of poly(p-chlorostyrene)

[0130] A 28.4 mg quantity (0.10 mmole) of the 1-chloro-4-(1-methylallyl-ethyl)benzene prepared in Preparation Example 5, 1.39 g (10 mmoles) of p-chlorostyrene and a solution of 28.5 mg (0.10 mmole) of the dimethyl diellulide prepared in Preparation Example 3 were stirred at 100°C for 10 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(p-chlorostyrene) in a yield of 77%.

#### Example 20

##### Preparation of poly(methyl vinyl ketone)

[0132] A 25.8 mg quantity (0.10 mmole) of the ethyl-2-methyl-2-methylallyl-propionate prepared in Preparation Example 2, 0.70 g (10 mmoles) of methyl vinyl ketone and a solution of 28.5 mg (0.10 mmole) of the dimethyl diellulide prepared in Preparation Example 3 were stirred at 80°C for 48 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl vinyl ketone) in a yield of 21%.

[0133] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 7800 and PD=1.25.

#### Example 21

##### Preparation of poly(methacrylonitrile)

[0134] A solution of 25.8 mg quantity (0.10 mmole) of the ethyl-2-methyl-2-methylallyl-propionate prepared in Preparation Example 2, 0.671 mg (10 mmoles) of methacrylonitrile, 25.5 mg (0.10 mmole) of the dimethyl diellulide prepared in Preparation Example 3 and 0.5 ml of dimethylformamide (DMF) were stirred at 80°C for 48 hours within a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methacrylonitrile) in a yield of 48%.

#### Example 22

##### Preparation of poly(N-methyl methacrylamide)

[0135] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 5800 and PD=1.09.

#### Example 23

##### Preparation of poly(N-methyl methacrylamide)

[0137] GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)) revealed Mn 9300 and PD=1.18.

#### Example 24

##### Preparation of poly(N-methyl methacrylamide)

[0138] Methyl methacrylate [stabilized with hydroquinone (HQ)] and a solution of the dimethyl diellulide prepared in Preparation Example 3 were stirred in the ratio listed in Table 2 along with 25.8 mg (0.10 mmole) of the ethyl-2-methyl-2-methylallyl-propionate prepared in Preparation Example 2 in a glove box having its inside air replaced by nitrogen. After the completion of the reaction, a portion of the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 250 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate).

#### Example 25

##### Preparation of poly(methyl methacrylate)

[0139] Table 2 shows the result of GPC analysis (with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)).

Ex.	methyl methacrylate	dimethyl diellulide	reaction condition	yield (%)	Mn	PD
23	10.1g (100mmol)	57.0mg (0.2mmol)	80°C, 10h	57.8	47000	1.19

Table 2

[0140] GPC analysis (with reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 7300 and PD=1.07.



methacrylate-*b*-tert-butyl acrylate) diblock polymer in a yield of 57%. GPC analysis revealed Mn 17300 and PD=1.11.

**Example 32**

**Preparation of poly(tert-butyl acrylate-*b*-methyl methacrylate) diblock polymer**

[0154] A 1.28 g quantity (10 mmole) of 1-butyl acrylate and 24.8 mg (0.10 mmole) of the (1-methylallyl-ethyl) benzene prepared in Preparation Example 1 were reacted at 100°C for 24 hours in a glove box having its inside air replaced by nitrogen. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of deuteriochloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording a poly(methyl methacrylate-*b*-tert-butyl acrylate) diblock polymer in a yield of 85%. GPC analysis revealed Mn 7600 and PD=1.15.

[0155] Next, 0.05 mmole of the poly(1-butyl acrylate) used as a macronitiator obtained above and 0.05 g (5 mmole) of methyl methacrylate, 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 and 2 ml of trifluoromethylbenzene were reacted at 100°C for 18 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(tert-butyl acrylate-*b*-methyl methacrylate) diblock polymer in a yield of 88%. GPC analysis revealed Mn 19500 and PD=1.35.

**Example 33**

**Preparation of poly(methyl methacrylate-*b*-tert-butyl acrylate-*b*-methyl methacrylate) triblock polymer**

[0156] A 1.01 g quantity (10 mmole) of methyl methacrylate, 24.8 mg (0.10 mmole) of the (1-methylallyl-ethyl) benzene prepared in Preparation Example 1 and 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 were reacted at 80°C for 15 hours in a glove box having its inside air replaced by nitrogen. Subsequently, 1.28 g (10 mmole) of 1-butyl acrylate was added to the reaction mixture and reacted therewith at 100°C for 35 hours (Mn 11500, PD=1.09). Then added to the reaction mixture were 3.9 g (23 mmole) of styrene and 5 ml of trifluoromethylbenzene, and the mixture was reacted at 100°C for 15 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording poly(methyl methacrylate-*b*-tert-butyl acrylate-*b*-methyl methacrylate) triblock polymer in a yield of 69%. GPC analysis revealed Mn 21600 and PD=1.27.

**Example 34**

**Preparation of poly(methyl methacrylate-*b*-styrene-*b*-tert-butyl acrylate) triblock polymer**

[0157] A 1.01 g quantity (10 mmole) of methyl methacrylate, 24.8 mg (0.10 mmole) of the (1-methylallyl-ethyl) benzene prepared in Preparation Example 1 and 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 were reacted at 80°C for 15 hours in a glove box having its inside air replaced by nitrogen. Subsequently, 1.04 g (10 mmole) of styrene was added to the reaction mixture and reacted therewith at 100°C for 24 hours (Mn 18700, PD=1.18). Then added to the reaction mixture were 3.85 g (30 mmole) of tert-butyl acrylate and 3 ml of trifluoromethylbenzene, and the mixture was reacted at 100°C for 24 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording a poly(methyl methacrylate-*b*-styrene-*b*-tert-butyl acrylate) triblock polymer in a yield of 45%. GPC analysis revealed Mn 21900 and PD=1.18.

**Example 35**

**Preparation of poly(styrene-*b*-methyl methacrylate-*b*-tert-butyl acrylate) triblock polymer**

[0158] A 1.04 g quantity (10 mmole) of styrene, 24.8 mg (0.10 mmole) of the (1-methylallyl-ethyl)benzene prepared in Preparation Example 1 were reacted at 100°C for 20 hours in a glove box having its inside air replaced by nitrogen. Subsequently, 1.01 g (10 mmole) of methyl methacrylate and 28.5 mg (0.10 mmole) of the dimethyl ditelluride prepared in Preparation Example 3 were added to the reaction mixture and reacted therewith at 80°C for 16 hours (Mn 12700, PD=1.30). Then added to the reaction mixture were 3.85 g (30 mmole) of tert-butyl acrylate and 3

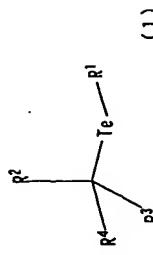
ml of trifluoromethylbenzene, and the mixture was reacted at 100°C for 24 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was thereafter poured into 300 ml of hexane being stirred. The resulting polymer precipitate was collected by suction filtration and dried, affording a poly(methyl methacrylate-*b*-styrene-*b*-tert-butyl acrylate) triblock polymer in a yield of 32%. GPC analysis revealed Mn 16110 and PD=1.27.

**INDUSTRIAL APPLICABILITY**

[0159] The invention provides a process for preparing living radical polymers which realizes precision control of molecular weights and molecular weight distributions under mild conditions. The living radical polymers obtained by the polymerization process of the invention readily permit conversion of terminal groups to other functional groups, are useful for preparing macromonomers and useful as compatibilizing agents and as materials for block polymers.

**Claims**

1. A process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2)



wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>8</sub> alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom or C<sub>1</sub>-C<sub>8</sub> alkyl, and R<sup>4</sup> is aryl, oxy carbonyl or cyano

(1) 
$$(R^1Te)_2$$
 (2)

wherein R<sup>1</sup> is the same as above.

40 2. A process according to claim 1 wherein R<sup>1</sup> in the living radical polymerization initiator represented by the formula (1) is C<sub>1</sub>-C<sub>4</sub> alkyl, phenyl, pyridyl, furyl or thiényl, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom or C<sub>1</sub>-C<sub>8</sub> alkyl, and R<sup>4</sup> is phenyl, naphthyl, pyridyl, furyl, thiényl, methoxycarbonyl, ethoxycarbonyl or cyano.

45 3. A process according to claim 1 wherein R<sup>1</sup> in the living radical polymerization initiator represented by the formula (1) is C<sub>1</sub>-C<sub>4</sub> alkyl, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom or C<sub>1</sub>-C<sub>4</sub> alkyl, and R<sup>4</sup> is phenyl, substituted phenyl, methoxycarbonyl or ethoxycarbonyl.

50 4. A process according to claim 1 wherein R<sup>1</sup> in the compound represented by the formula (2) is C<sub>1</sub>-C<sub>4</sub> alkyl, phenyl, naphthyl, pyridyl, furyl or thiényl.

55 5. A process according to claim 1 wherein R<sup>1</sup> in the compound represented by the formula (2) is C<sub>1</sub>-C<sub>4</sub> alkyl or phenyl.

6. A living radical polymer obtained by polymerizing a vinyl monomer with use of a living radical polymerization initiator represented by the formula (1) and a compound represented by the formula (2).

7. A mixture of a living radical polymerization initiator represented by the formula (1) and a compound represented

by the formula (2).

8. A mixture according to claim 7 wherein the living radical polymerization initiator represented by the formula (1) is an organotellurium compound represented by the formula (1) wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>4</sub> alkyl, R<sub>2</sub> and R<sub>3</sub> are each a hydrogen atom or C<sub>1</sub>-C<sub>4</sub> alkyl, and R<sub>4</sub> is aryl, substituted aryl or oxy carbonyl, and the compound represented by the formula (2) is a compound wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>4</sub> alkyl or phenyl.

9. A process for producing a diblock copolymer wherein in a compound of the formula (1) and a compound of the formula (2) are used when a homopolymer is prepared from the first of monomers and/or when the diblock copolymer is subsequently prepared.

10. A process for producing a triblock copolymer wherein in a compound of the formula (1) and a compound of the formula (2) are used at least once when a homopolymer is prepared from the first of monomers, or when a diblock copolymer is subsequently prepared, or when the triblock copolymer is subsequently prepared.

11. A process for producing a diblock copolymer comprising mixing together an (meth)acrylic acid ester monomer, a living radical polymerization initiator represented by the formula (1) and a compound of the formula (2) to prepare a poly(meth)acrylate, and subsequently mixing an aromatic unsaturated monomer with the product to obtain an (meth)acrylate-aromatic unsaturated monomer diblock copolymer.

12. A process for producing a triblock copolymer comprising mixing together an (meth)acrylic acid ester monomer, a living radical polymerization initiator represented by the formula (1) and a compound of the formula (2) to prepare a poly(meth)acrylate, subsequently mixing an aromatic unsaturated monomer with the product to obtain an (meth)acrylate-aromatic unsaturated monomer block copolymer, and subsequently mixing an (meth)acrylic acid ester monomer or aromatic unsaturated monomer with the copolymer to obtain the triblock copolymer.

13. A process according to any one of claims 1 to 5 wherein the vinyl monomer is at least one monomer selected from the group consisting of (meth)acrylic acid ester monomer, aromatic unsaturated monomer (styrene type monomer), carboxyl-containing unsaturated monomer, (meth)acrylonitrile and (meth)acrylamide type monomer.

14. A process according to any one of claims 1 to 5 wherein the living radical polymer is a random copolymer.

15. A process according to any one of claims 1 to 5 wherein the living radical polymer is a block copolymer.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/10116

A. CLASSIFICATION OF SUBJECT MATTER  
Int.-Cl? C08F4/00, C08F29/00

According to International Patent Classification (IPC) or to both national classifications and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
Int.-Cl? C08F4/00-4 / 82

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Jitsuya Shibusawa Koho 1926-1956 Jitsuya Shiran Toroku Koho 1996-2003  
Kokai, Jitsuya Shibusawa Koho 1971-2003 Toroku Jitsuya Shiran Koho 1994-2003  
External databases consulted during the International search (names of data base end, where practicable, search terms used)  
CR (SPN), REGISTRY (STN)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Character of document, with indication, when appropriate, of the relevant passages	Relevant to claim No.
P,X	Shigeru YANAGO et al., "Tailored Synthesis of Structurally Defined Polymers by Organotellurium-Mediated Living Radical Polymerization (TERP)", Journal of the American Chemical Society, 20 November, 2002 (20.11.02), Vol.124, No. 46, pages 13666 to 13667	1-15
A	Shigeru YANAGO et al., "Organotellurium Compounds as Novel Initiators for Controlled Living Radical Polymerizations", Journal of the American Chemical Society, 27 March, 2002 (27.03.02), Vol.124, No.12, pages 2814 to 2815	1-15

Further documents are listed in the continuation of Box C.  See patent family annex.

Special criteria of cited documents:  
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"T" earlier document but published on or after the international filing date.  
"I" document which may throw doubt on a priority claim(s) or which is cited to establish the publication date of another document or which is relevant to determine the particular relevance of the claimed invention, cannot be considered to involve an inventive step in the inventive situation when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"R" document published earlier than the international filing date but later than the priority date claimed.  
Date of file actual completion of the International search report 05 September, 2003 (05.09.03)

Date of mailing of the International search report 16 September, 2003 (16.09.03)

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